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ANALYZING SYSTEM FOR THE DETECTION OF REDUCING AND OXIDIZING GASES IN A CARRIER
GAS WITH A METAL-OXIDE-SEMICONDUCTOR SENSOR ARRANGEMENT

5 This invention relates to an analyzing system for the
detection of reducing and oxidizing gases and the real-
time control of the quality of a carrier gas flow. It also
relates to the utilization, in the absence of oxygen, of
gas sensors based on semiconductor-type metal oxides.
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BACKGROUND OF THE INVENTION

The most usual technique for assessing the quality of a
carrier gas, such as carbon dioxide, involves the use of
15 specific chromatography equipment, which include various
types of detectors to ensure the sensitivity and
selectivity of analysis of the habitual contaminants
present in carbon dioxide. In addition to being expensive,
such equipment has the disadvantage of not permitting
20 continuous monitoring of the gas being used in production.
Such pieces of equipment only carry out ad hoc sample
analysis. This technique is used habitually in production
centers to evaluate the quality of the dioxide obtained,
but as such equipment is expensive it can hardly be
25 installed in any plant that consumes carbon dioxide, such
as a carbonated drinks bottling plant. One alternative is
to take ad hoc samples that can be sent to the pertinent
laboratory for analysis. However, this system does not
permit continuous monitoring of the gas flow, while the
30 costs involved therein are far from negligible.
 Known in the market are analyzing systems for
analyzing the quality of carbon dioxide, comprising
various types of specialized equipment such as:
 • sulfur compounds analyzers, generally based on
35 pyro-luminiscence systems;

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- aromatic hydrocarbon analyzers, based on PID (Photo Ionization Detector) systems with ultraviolet-light lamp;
- total hydrocarbons analyzers, based on FID (Flame Ionization Detector) systems.

5   Such analysis systems have the disadvantage of being expensive for installing in carbon dioxide consuming plants, while neither do they permit the carrying out of a real-time analysis of a continuous flow of carbon dioxide.

10   There exists in the market no low-cost system capable of carrying out an (even partial) real-time analysis of the quality of carbon dioxide.

None of the habitual techniques used for evaluating the quality of carbon dioxide is based on the
15 utilization of sensors based on semiconductor-type metal oxides.

Known in the art are gas sensors based on semiconductor-type metal oxides for the detection of gases such as toxic gases in the atmosphere. These are simple,
20 low-cost and robust sensors.

Sensors based on semiconductor-type metal oxides have been developed for the detection of reducing and oxidizing gases in the presence of pure air and, therefore, in the presence of oxygen.

25   It is known that in the presence of pure air the active material or semiconductor metal oxide (type n), when heated to a temperature between 300°C and 500°C, adsorbs atmospheric oxygen until it reaches a state of equilibrium. The process of adsorption of an oxygen atom
30 involves the taking up of an electron from the conduction band of the metal oxide. Therefore, when a sensor is in the presence of pure air and in equilibrium, it shows high electrical resistance, also called base resistance.

It is known that if the sensor is exposed to the
35 presence of a reducing gas, the gas will react with the

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adsorbed oxygen, once again establishing a state of equilibrium. In this case, the concentration of adsorbed oxygen atoms will be lower than that which existed in the presence of pure air, and this will show itself in a
5 larger number of electrons on the conduction band. This results in a very marked reduction of sensor resistance. This effect is reversible, for the sensor can recover its base resistance if it is once again exposed to the presence of pure air.

10   In the presence of an oxidizing gas, competition arises around the adsorption sites between that gas and the oxygen. This shows itself in new state of equilibrium in which the sensor resistance increases. This effect is in turn reversible.

15   It is known that the operational principle of the type of sensors described can be summarized in that the conductance of such devices changes progressively with the changes that take place in the composition of the atmosphere.

20   No sensors are known, however, based on semiconductor-type metal oxides that permit the detection of reducing and oxidizing gases in the complete absence of oxygen in a carrier gas atmosphere or current.

25 DESCRIPTION OF THE INVENTION

The objective of this invention is to solve the disadvantages mentioned by developing an analyzing system for the detection of reducing and oxidizing gases in a
30 carrier gas which evaluates the quality of the carrier gas in real time, by using gas sensors based on semiconductor-type metal oxides that work in the absence of oxygen.

In accordance with this objective, the analyzing system of this invention comprises a plurality of
35 detecting means, calibrating means, means for processing

and control of acquisition and data recognition, and is characterized in that said gas-detection means are sensors based on semiconductor-type metal oxides that work in the absence of oxygen, in that said system includes means for
5 connecting said carrier gas to a measuring chamber which contains said sensors, and in that said means of processing and control include a system of real-time recognition of said gases, which provides a diagram with delimited decision zones, in which the measurements taken
10 on said carrier gas are situated and identified.

Thanks to its characteristics, the analyzing system permits the carrying out of real-time analysis of the quality of a carrier gas, such as carbon dioxide. This is low-cost equipment that can be applied in plants that
15 consume gases, such as carbon dioxide, as in carbonated drinks bottling plants.

In accordance with the invention, the system is characterized in that said calibration means include a plurality of patterns or calibrated gases at least equal
20 in number to the number of reducing and oxidizing gases that have to be detected in the carrier gas, and in that the response of the plurality of sensors to the measurements of said patterns includes the obtaining of a vector of conductance variation for each calibrated gas or
25 standard.

In accordance with the invention, said recognition system comprises obtaining a learning matrix resulting from grouping the conductance variation vectors of the measurements taken with the plurality of patterns or
30 calibrated gases.

In accordance with the objective of this invention, said recognition system identifies the measurements taken in the carrier gas, according to the algorithm:

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- obtaining a vector of conductance variation for the plurality of sensors that make up the system.
- auto scaling of the vector with the mean values and variances used to auto scale the learning matrix obtained from the patterns or calibrated gases.
- projecting the auto scaled vector onto the space of the principal components extracted on the basis of the learning matrix obtained with the calibration means.
- depending on the position occupied by said vector, the system identifies a type of response.

Preferably, the type of response identified by the system includes the responses of pure carrier gas, contaminated carrier gas at alert level due to at least one contaminant and contaminated carrier gas at alarm level due to at least one contaminant.

Advantageously, the system is characterized in that said processing and control means include a microprocessor that corrects temporary deviations of the sensor responses and controls and processes the data that permit detection of the presence of reducing and/or oxidizing gases at various pre-established levels.

Preferably, said connecting means comprise a plurality of electrically operated valves and connecting pipes to permit the carrier gas or calibrated gases to flow through the chamber that contains the sensors.

According to a preferred embodiment of the invention, the carrier gas is carbon dioxide.

In accordance with the invention, the utilization of a gas sensor based on semiconductor-type metal oxides is proposed for detecting reducing and oxidizing gases present in a carrier gas, in the absence of oxygen.

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Absence of oxygen in the carrier gas refers here
to oxygen values in said gas not exceeding 30 ppm of
oxygen.

5 BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of the matters described, some
drawings are attached which, schematically and solely by
way of non-restrictive example, show a practical case of
10 embodiment.

In said drawings,

Figure 1 shows the response of two sensors based
on tin oxide to 15 ppm of methane diluted in carbon
dioxide (Figure 1a) and 1 ppm of sulfur dioxide diluted in
15 carbon dioxide (Figure 1b).

Figure 2 shows a block diagram of operation of the
analyzing system.

Figure 3 shows a diagram or space of the principal
components with zones or areas of decision delimited for
20 pure carbon dioxide, carbon dioxide at alert level and
carbon dioxide at alarm level.

Figure 4 shows a diagram or space of the principal
components on which three measurements taken on the carbon
dioxide have been projected, corresponding to the three
25 vectors I_1, I_2 and I_3.

DESCRIPTION OF A PREFERRED EMBODIMENT

Figures 1a and 1b show the response of two gas sensors
30 based on tin dioxide (type-n semiconductor) to the
presence of traces of methane and of sulfur dioxide,
respectively, diluted in carbon dioxide.

The gas sensors based on semiconductor-type metal
oxides of this invention detect oxidizing and reducing
35 gases in a continuous current of carbon dioxide, in the

absence of oxygen, that is, at an oxygen concentration in the carbon dioxide at levels not exceeding 30 ppm of oxygen.

Figure 1a of this invention shows the response 1
5 of a sensor based on tin oxide (type-n semiconductor) to 15 ppm of methane diluted in carbon dioxide, together with the base resistance 2 of the same sensor when in a state of equilibrium with the carbon dioxide. The presence of the reducing gas leads to a decrease of sensor 2
10 resistance. This effect is reversible, since the sensor can recover its base resistance 2 if the reducing gas, in this case methane, is eliminated and the sensor once again exposed to the carbon dioxide. Figure 1b of this invention shows the response 3 of another sensor based on tin oxide
15 (type-n semiconductor) to 1 ppm of sulfur dioxide diluted in carbon dioxide, together with the base resistance 4 of the same sensor when in a state of equilibrium with the carbon dioxide. In this case, the presence of an oxidizing gas leads to an increase in the resistance 4 of the
20 sensor. This effect is again reversible.

It has been observed that carbon dioxide interacts reversibly with the surface of the metal oxide, acting in a similar way to oxygen in the detection of traces of contaminants (reducing and oxidizing gases).

25   Gas sensors in general, and sensors based on metal oxides in particular, are not very selective. This means that all the sensors show different, though not nil, responses to the contaminant gases. It is therefore necessary to use an array of several sensors based on
30 metal oxides, with partially overlapping sensitivities, in order to be able to identify the various contaminant gases in the carbon dioxide.

Figure 2 of this invention shows a block diagram that facilitates understanding of the functioning of the
35 analyzing system. Said system consists in a measuring

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chamber, made of stainless steel, which contains seven
sensors 23 based on metal oxides, provided with different
catalytically active noble metals. The number of sensors
bears a relationship with the number of contaminant gases
5 that must be detected in the carrier gas 21 or carbon
dioxide whose quality is to be evaluated. In the example
in question, the sensors were chosen for detecting gases
such as methane, propane, butane, hexane and other organic
compounds, such as ethylene. The system includes means of
10 connecting 22 the carbon dioxide 21 to the measuring
chamber, which contains the sensors 23. These consist in a
variable number of electrically operated valves, made of
stainless steel, to permit the gas whose quality is to be
evaluated, or else different calibrated gases 26 or
15 calibration patterns, to flow through the chamber in which
the sensors 23 are located. The flow of the gases must be
set to a constant value, preferably 100 ml/min.

The resistance reading of the sensors is
implemented by means of a semi-bridge of resistances, in
20 which one resistance is the sensor (Rs) itself and the
other is a fixed resistance (Rm) of appropriate value. A
known voltage (Vc) is applied to both resistances
connected in series and the voltage is measured at the
intermediate point (Vm). This voltage is converted from
25 analog voltage to digital voltage by an analog-digital
converter A/D.

The sensors are heated by means of electronic
circuits which permit the sensors to be heated up to their
optimum operational temperature (between 300 and 400°C).
30   A program implemented by a microprocessor 24
carries out the following functions:

a) Control of the electrically operated valves
during both the normal measuring phase and the equipment
calibration phase.

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b) Control of the process of taking up the Vm voltages and their A/D conversion.

c) Obtaining the voltage Vm for each sensor in the bank, once each second, and calculating the average of the Vm values over the course of one minute. For each sensor, therefore, the average Vm values are from then on calculated on the basis of the last sixty measurements taken.

d) Obtaining the resistances for each one of the sensors in the bank, using the average of the Vm values. Thus, with the average Vm_i value known, the resistance R_i for the i-nth sensor in the bank is obtained by means of the calculation:

$R_i = VcR_m / (Vc - Vm_i)$

e) Calculating the conductance values, once the resistance values of the sensors have been calculated. The conductance value variation ΔG_i for the i-nth sensor is defined by means of the expression: $\Delta G_i = 1/R_i - 1/R_{oi}$, where R_{oi} is the resistance of the sensor in the presence of the pure gas analyzed, or base resistance of the i-nth sensor.

f) Obtaining the vector of conductance variation for each measurement; vector $I = (\Delta G_i, ..., \Delta G_n)$, where n is the number of sensors making up the bank. Said vector constitutes the starting information for a recognition algorithm, which then evaluates the quality of the gas being analyzed.

g) Periodic downloading of the information generated by the analyzing system to an Internet address. If levels of any contaminant above preset values are detected, the system can send alert and/or alarm messages to mobile telephones.

The analyzing system described includes a data-recognition system 24 based on a learning process that takes measurements using a set of patterns or calibrated

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gases 26. The response of the recognition 24 system will be one of the following three:

a) Pure carbon dioxide identified.

b)   Contaminated   carbon   dioxide   at   alert-level
5 concentration identified. The contaminant(s) is(are) as follows: list of contaminants.

c)   Contaminated   carbon   dioxide   at   alarm-level concentration identified. The contaminant(s) is(are) as follows: list of contaminants.

10   The   learning   process   consists   in   taking measurements using a set of patterns or calibrated gases 26. The patterns consist in pure carbon dioxide and contaminated carbon dioxide. Two calibrated patterns are used for each contaminant considered: one standard with 15 the contaminant diluted to the alert concentration of carbon dioxide and the other diluted to the alarm concentration. Finally, patterns with binary mixtures of contaminants are also used. Each measurement is repeated at least three times in order to achieve a representative 20 set of measurements. This learning process makes it possible to achieve a learning matrix, A, resulting from grouping together the conductance variation vectors obtained in response to the learning measurements described above. The dimension of A is mxn, where m (rows) 25 is the number of learning measurements and n (columns) is the number of sensors forming part of the bank. Thus, each of the rows of A corresponds to one of the learning measurements, and each of the columns of A contains the conductance variations undergone by one sensor of the 30 bank.

The matrix A is standardized by means of an auto scaling operation. This operation is carried out by columns. The mean and the standard deviation of each column are obtained. If M_i and D_i are, respectively, the 35 mean and the standard deviation of column i, then the new

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value of any element of that column is calculated as a new
by means of $e_{ki} = (e_{ki} - M_i) / D_i$, where e_{ki} represents the
element of row k, column i in matrix A. Once A has been
auto scaled, an extraction of principal components is
5 carried out. The principal component extraction process is
a standard technique not described here. The principal
components are made up of a linear combination of the
columns of the auto scaled matrix A.

The result of the extraction of principal
10 components carried out on a set of measurements with
patterns or calibrated gases is a diagram 25 of arbitrary
units in which those measurements are situated. The last
step in the learning process consists in defining decision
boundaries between the zones of pure carbon dioxide,
15 contaminated carbon dioxide at alert level and
contaminated carbon dioxide at alarm level.

Figure 3 shows a diagram 25 with decision zones or
areas delimited for pure carbon dioxide, contaminated
carbon dioxide at alert level and contaminated carbon
20 dioxide at alarm level. Said diagram 25 was obtained with
the learning process by using the measurements with the
calibrated gases or patterns 26. Reference 00 relates to a
measurement with pure carbon dioxide, while references 01,
02, 03, 04, 05, 06, 14 and 32 relate to measurements of
25 carbon dioxide with different types or mixtures of
contaminants.

In Figure 3:

00: pure CO2

01: CO2 + 10 ppm ethylene

30   02: CO2 + 20 ppm ethylene

03: CO2 + 30 ppm methane

04: CO2 + 15 ppm methane

05: CO2 + 0.5 ppm sulfur dioxide

06: CO2 + 1 ppm sulfur dioxide

35   14: CO2 + 10 ppm ethylene + 15 ppm methane

32: CO_2 + 20 ppm ethylene + 30 ppm methane

In said diagram 25, it can be observed that the pure carbon dioxide is clearly differentiated from the contaminated carbon dioxide. Different types of
5 contamination are also observable, since the measurements of a single type, for example pure carbon dioxide, appear grouped in the space of the first two principal components, while the measurements of carbon dioxide affected by different contaminants occupy different
10 positions in the space from the first two principal components.

The data recognition system 24 described identifies the measurements taken in the carrier gas 21, in this case carbon dioxide, according to the algorithm:
15 a) Obtaining of a new conductance-variation vector or new measurement that has to be identified.

b) Auto scaling of the vector, using the means and variances used to auto scale the learning matrix A.

c) Projection of the auto scaled vector on the space of
20 the principal components.

d) Depending on the position occupied by said vector, the system decides which type of outlet has been identified.

Figure 4 shows a diagram or space 25 of the principal components onto which three measurements have
25 been projected, corresponding to the three vectors I_1, I_2 and I_3. These measurements must be identified by the recognition system 24. Given the position occupied by projection I_1, it is concluded that said measurement pertains to pure carbon dioxide. The position of I_2 is
30 very close to that of the calibration measurements with methane, so it is concluded that this measurement corresponds to an alert level due to methane contamination in the carbon dioxide. The position of I_3 is very close to that of the calibration measurements with methane and
35 ethylene, so it is concluded that this measurement

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corresponds to an alarm level due to methane and ethylene contamination in the carbon dioxide.

The gas sensors 23 suffer from temporary deviations in their response. These deviations can be 5 associated with raw material ageing processes. Therefore, in order to maintain the analyzing system in good operational order over time calibrations have to be carried out periodically. The system implements these calibrations in an automated way transparent to the 10 user/operator. At preset intervals, such as every twenty-four hours, the system enters self-calibration mode. In this mode the following steps are carried out:

a) Taking a measurement with each of the calibrated patterns: pure carbon dioxide, carbon dioxide with 15 contaminant alarm level 1, carbon dioxide with contaminant alarm level p, where p is the number of contaminants detected in the carbon dioxide.

b) Auto scaling and projection of the calibration measurements onto the space 25 of the principal 20 components.

c) Reckoning of the distances of each of the calibration measurements from the centroid of the class to which they belong. If that distance exceeds a certain preset measurement, new decision boundaries are recalculated 25 taking account of the information provided by the calibration measurements.

Once the self-calibration process has ended, the equipment is ready to proceed with the real-time analysis of the quality of the carbon dioxide or carrier gas.

30 Although one specific embodiment of the invention has been described and shown, it will be clear that an expert on the subject could introduce variations and modifications, or replace the details with others that are technically equivalent, without departing from the sphere 35 defined by the attached claims.